

ATOMIC OXYGEN EFFECTS ON CANDIDATE COATINGS FOR LONG-TERM SPACECRAFT IN LOW EARTH ORBIT

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ABSTRACT

Candidate atomic oxygen protective coatings for long-term low Earth orbit (LEO) spacecraft have been evaluated using the Los Alamos National Laboratory O-atom exposure facility. The coatings studied include Teflon, Al_2O_3 , SiO_2 , and SWS-V-10, a silicone material. Preliminary results indicate that sputtered PTFE Teflon ($0.1 \mu\text{m}$) has a fluence lifetime of 10^{19} O-atoms/ cm^2 , and sputtered silicon dioxide ($0.1 \mu\text{m}$), aluminum oxide ($0.1 \mu\text{m}$), and SWS-V-10, a silicone, ($4 \mu\text{m}$) have fluence lifetimes of 10^{20} to 10^{21} O-atoms/ cm^2 . There are large variations in fluence lifetime data for these coatings. Further investigations are under way to determine the failure mechanisms.

INTRODUCTION

The low Earth orbit (LEO) environment is known to react with many spacecraft materials, especially organic polymers.^{1,2} Samples retrieved from Space Shuttle flights after being exposed to LEO had mass loss as well as surface morphology changes. The primary constituent of the LEO environment at Space Shuttle altitudes, atomic oxygen, is suspected to be the principal cause of the erosion of materials because of its high oxidative ability, flux (10^{15} atoms/ cm^2 -sec) and collision energy (5 eV) for a spacecraft traveling at 8 km/sec.

Spacecraft for long duration missions such as the Space Station must utilize materials that can withstand the environment without undergoing significant changes in material properties. Reactive materials must be coated with a protective coating if they are to achieve longevity in LEO. A variety of protective coatings, such as ion-beam sputter-deposited thin films,³ silicones and Teflon⁴ have been proposed and developed for extended use in LEO. Some of these coatings have been tested on Space Shuttle flight experiments, but Space Shuttle flight data provide only limited information on the feasibility of long-term use of these materials in LEO. Space Shuttle flight experiments provide relatively small fluence exposures (10^{20} O-atoms/ cm^2) in comparison to the exposure a spacecraft such as Space Station will experience during 20-30 years in LEO (10^{22} - 10^{23} O-atoms/ cm^2).¹ It is, therefore, necessary to evaluate materials using ground-based simulation facilities which can perform accelerated testing at flux levels up to 10^{17} O-atoms/ cm^2 -sec.

INSTRUMENTATION

The Los Alamos National Laboratory O-atom source^{5,6} uses a CW plasma produced by focusing a high power CO₂ laser beam in a hydrodynamic expansion nozzle that has an oxygen/rare gas mixture flowing into it. The resulting temperature of the plasma is about 15,000° K. Using argon or neon as the rare gas, the percentage dissociation of molecular oxygen into atomic oxygen is about 85%. The facility is capable of producing atomic oxygen fluxes of up to 10¹⁷ O-atoms/cm²-sec, energies of 1-5 eV, and total fluences of 10²² O-atoms/cm².⁶

TECHNIQUE TO EVALUATE COATINGS

A technique to evaluate candidate coatings for atomic oxygen resistance has been developed, which uses silver oxidation as an atomic oxygen detector.⁷ Silver oxidizes to silver oxide in the presence of atomic oxygen, and the electrical resistance of the oxide is dramatically higher than that of pure silver. Coatings of known thicknesses are deposited on top of a thin (250 Å) silver film and as atomic oxygen penetrates or diffuses through the coatings, the measured electrical resistance increases. The technique has been demonstrated to be highly sensitive to atomic oxygen and can also provide quantitative measurements of atomic oxygen flux.⁶ A schematic of the sensor is shown in figure 1.

Samples are mounted on a sample manipulator and accurately placed perpendicular to the O-atom beam axis. Electronic instrumentation was arranged so that continuous in-situ resistance measurements can be obtained during atomic oxygen exposure. Figure 2 shows the resistance-measuring circuit for the actinometers. A constant current is supplied to the silver films and resistance data is obtained through voltage measurements. A high impedance voltage-to-frequency converter feeds a multichannel analyzer, which stores the voltage measurements as a function of exposure time. The data is then fed to a computer for data analysis.

SAMPLE PREPARATION

The actinometers were coated with PTFE Teflon, Al₂O₃, SiO₂, and silicone SWS-V-10 materials. The PTFE Teflon was sputtered using a Teflon target at the NASA-Lewis Research Center. The thicknesses of the PTFE Teflon coatings were 800 Å and 1250 Å, as determined by performing profilometry on separate witness samples. The Al₂O₃ and SiO₂ coatings were sputtered using Al₂O₃ and SiO₂ targets at the MDAC-HB facility. The Al₂O₃ and SiO₂ coatings were 950 Å, as determined by performing ellipsometry on witness silicon wafer samples. We estimate the measured thicknesses of all the sputtered coatings to be within ±10%. The SWS-V-10 silicone coating was brushed on at NASA-Marshall Space Flight Center. The thickness of the brushed coating is estimated to be between 4 and 10 μm. For data analysis of these samples, we will assume that the coatings had a thickness of 4 μm.

O-ATOM BEAM FLUX CALIBRATION

The time history of oxidation of 250 Å thick bare silver films when exposed to the O-atom beam can be used to calculate the oxidation rate in monolayers/second, which can then be converted to a beam flux in atoms/cm²-sec. The oxidation rate and beam flux were calculated using the assumptions that: 1) the sticking probability of O-atoms on bare polycrystalline silver is unity over the entire range of oxide formation, 2) the nearest neighbor distance (NND) in polycrystalline silver is 2.9 Å, the same as that for the silver face centered cubic structure, and 3) the O₂ molecules in the beam (about 15%) do not react with silver to form silver oxide. The flux is then calculated from:

$$\text{Oxidation rate (monolayers/sec)} = \frac{\text{Thickness of Ag film (Å)}}{\text{Time of oxidation (sec)} \times \text{NND (Å/monolayer)}}$$

$$\text{Beam flux (atoms/cm}^2\text{-sec)} = \text{Oxidation rate} \times \text{No. of Ag atoms/cm}^2\text{-monolayer,}$$

where No. of Ag atoms/cm²-monolayer = 1.2×10^{15} , as determined from the NND.

In these experiments, when bare 250 Å thick silver films were placed 15 cm from the nozzle, the estimated atomic oxygen flux was 1×10^{17} atoms/cm²-sec. With the exception of Teflon, all of the coatings were exposed to an O-atom beam (using an O₂/Ar mixture) having a kinetic energy of 1.5 eV (Teflon 3 eV) and a flux of 1×10^{17} atoms/cm²-sec (Teflon 6×10^{16} atoms/cm²-sec).

RESULTS

An example plot of the electrical resistance/conductance of silver underlying a protective coating as a function of O-atom fluence is provided in figure 3. The shapes of the resistance/conductance vs. fluence graphs, however, do vary from coating to coating as well as from sample to sample of the same coating. Please see Table I for a summary of the results obtained for the coatings studied.

PTFE Teflon:

ESCA analysis of the sputtered PTFE Teflon coatings before exposure showed that their atomic concentration was 45% C and 55% F. Two PTFE Teflon-coated actinometers (800 Å and 1250 Å) were exposed to an O-atom beam (using an O₂/Ne mixture) having a 3 eV kinetic energy and 6×10^{16} atoms/cm²-sec flux. Visual examination of the beam spot on the actinometers after O-atom exposure indicated that the Teflon was eroded away. Bulk Teflon has been tested in the LANL O-atom beam and profilometry measurements after exposure indicate there is erosion of Teflon through reaction with atomic oxygen. The PTFE Teflon tested at 3 eV kinetic energy gave a reaction efficiency of 0.22×10^{-24} cm³/atom for the 800 Å sample and 0.82×10^{-24} cm³/atom for the 1250 Å sample. Previous exposure of a 800 Å thick PTFE Teflon-coated actinometer to a flux of 9×10^{15} atoms/cm²-sec at 1.5 eV kinetic energy (using an O₂/Ar mixture) gave a reaction efficiency of 0.13×10^{-24} cm³/atom. The fluxes used in the Teflon exposures were reduced because of reduced gas flows in the nozzle.

Al₂O₃:

Auger analysis of the Al₂O₃ coating before exposure showed an atomic concentration of 33% Al, 65% O, and <2% C. SEM photographs of the coating up to a magnification of 20,000X did not reveal any obvious porosity. Two Al₂O₃-coated actinometers, both of 950 Å, were exposed to an O-atom beam (using an O₂/Ar mixture) having a 1.5 eV kinetic energy and 1.0×10^{17} atoms/cm²-sec flux. Complete oxidation of the underlying silver occurred after a fluence of 1.0×10^{20} atoms/cm² for one sample, whereas complete oxidation of the underlying silver occurred after a fluence of 8.3×10^{20} atoms/cm² for the other sample. Analyses of the Al₂O₃ coating after exposure are under way.

SiO₂:

Auger analysis of the SiO₂ coating before exposure showed an atomic concentration of 35% Si, 58% O, 5% N and 2% C. SEM photographs of the sputtered coating up to a magnification of 20,000X did not reveal any obvious porosity. Three SiO₂-coated (950 Å) actinometers were exposed under the same conditions as the Al₂O₃ samples. Complete oxidation of the underlying silver occurred after fluences of 1.2×10^{20} atoms/cm², 7.3×10^{20} atoms/cm², and 11.0×10^{20} atoms/cm². Visual inspection of the SiO₂-coated actinometers after the test runs indicated that the coating was still intact, and erosion of the coating as observed in the exposed PTFE Teflon samples did not occur.

ESCA and Auger analyses were performed on the SiO₂ coated silver strip after O-atom exposure and only a small percentage of silver (about 2%) was present on the sample surface. Auger elemental depth profile of a SiO₂-coated actinometer after exposure to a 11.0×10^{20} O-atom/cm² fluence is provided in figure 4. The profile confirms that the SiO₂ coating was not eroded away. There is a layer of SiO₂ on the surface, and silver does not appear until part of the coating is sputtered away. The profile does show, however, silver over a broad depth range, which may be due to the high surface roughness of the alumina substrate (>1 μm) and/or diffusion of silver into the coating.

SWS-V-10 Silicone:

The three SWS-V-10 silicone-coated actinometers (4 μm thickness) tested under the same conditions as the Al₂O₃ and SiO₂ samples showed complete oxidation of the underlying silver after fluences of 1.8×10^{20} atoms/cm², 4.9×10^{20} atoms/cm², and 6.0×10^{20} atoms/cm². Visual inspection of the silicone samples after exposure indicated that the coating was also intact, although the underlying silver had oxidized. Further analysis of these samples will be performed by NASA/MSFC.

DISCUSSION

The oxygen atom source provides, in addition to atomic oxygen, a flux of visible and infrared photons. With the exception of the PTFE Teflon-coated samples, which did not experience a temperature rise during the course of the

test runs, all of the other samples, aluminum oxide, silicon dioxide, and SWS-V-10 silicone, did experience sample heating. A thermocouple placed on the side of the sample substrate, but not in the beam spot, indicated that the substrates reached temperatures of up to 100° C by the end of the exposures. Readings from another thermocouple that was placed directly in the beam spot indicated that the beam spot temperature was another 20° C higher. The rate of temperature rise was not controlled.

Measurements of the vacuum UV (VUV) intensities⁶ produced by the plasma have been taken using a vacuum monochrometer with a CsTe solar blind and bialkali photomultiplier tubes. The 1.5-eV (O₂/Ar) beam produced VUV intensities about 3 times higher than that produced by solar radiation, while the 3-eV (O₂/Ne) beam produced VUV intensities about equal to solar VUV. The inorganic coatings (SiO₂ and Al₂O₃) are not likely to be affected by the VUV radiation, but organic coatings such as Teflon and silicones may degrade to the point where atomic oxygen has an enhanced reactivity with the photoproduct backbone of the polymer.

Auger analysis (figure 4) and visual inspection after exposure indicated that the SiO₂ coating was intact, although the underlying silver had oxidized. Diffusion of O-atoms into inorganic thin film coatings, therefore, may be a significant process that warrants additional attention. Since Auger analysis after exposure also revealed a broad distribution of silver in the thickness of the coated area, diffusion of silver into the coatings may have also occurred. Temperature effects could be significant in both of these processes.

The test results of the sputter-coated actinometers reveal a large scatter in the data (see table I), even though the coatings were coated during the same run and should be of the same thickness. Some of the parameters that would contribute to scatter in the data include temperature, coating continuity, coating impurities, and substrate surface roughness. Since the surface of the actinometers used in these experiments had roughness on the order of microns and the sputtered coatings were only about 0.1 μm in thickness, it is unknown whether continuous uniform coatings were protecting the actinometer surfaces. The quality of the coatings in terms of chemical composition and codeposited impurities is another factor to be considered in assessing their ability to protect reactive substrates. For future spacecraft parts, if thin film coatings are to be used, the ability to apply the coatings consistently on a large-scale basis and to certify the coating quality will be essential to ensure the substrate protection for the life of the spacecraft.

Of the coatings we tested to date (0.1 μm of sputtered Teflon, Al₂O₃, and SiO₂ and 4 μm of silicone), none of them have provided protection for the full atomic oxygen fluence of 10²² to 10²³ atoms/cm² expected for long-term spacecraft such as Space Station. Our results indicate that the coatings of the above-specified thicknesses may provide protection for O-atom fluences of 10²⁰ to 10²¹ atoms/cm². It is unclear at this point whether increasing the thickness of the coatings will proportionately increase the total O-atom fluence that these coatings can withstand. Future work will emphasize the fundamental mechanisms responsible for the interaction of these materials with O-atoms.

Of particular interest are thin film inorganic coatings and the relationship of diffusion-limited kinetics to the atomic oxygen kinetic energy.

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TABLE I. - SUMMARY OF COATINGS RESULTS

Coating	Thickness	Fluence Lifetime (Atoms/cm ²)
PTFE Teflon	800 Å	6.0 x 10 ¹⁹ (Reaction Efficiency of 0.13 x 10 ⁻²⁴ cm ³ /atom)
	800 Å	3.5 x 10 ¹⁹ (Reaction Efficiency of 0.22 x 10 ⁻²⁴ cm ³ /atom)
	1250 Å	1.5 x 10 ¹⁹ (Reaction Efficiency of 0.82 x 10 ⁻²⁴ cm ³ /atom)
Al ₂ O ₃	950 Å	1.0 x 10 ²⁰
	950 Å	8.3 x 10 ²⁰
SiO ₂	950 Å	1.2 x 10 ²⁰
	350 Å	7.3 x 10 ²⁰
	950 Å	11.0 x 10 ²⁰
SWS-V-10	4 μm	1.8 x 10 ²⁰
	4 μm	4.9 x 10 ²⁰
	4 μm	6.0 x 10 ²⁰

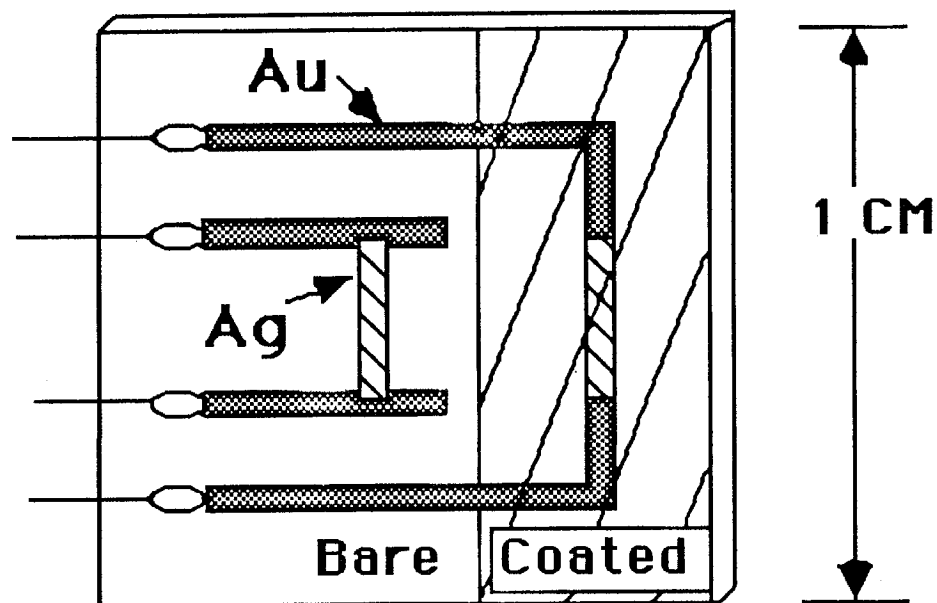


Figure 1. The O-atom actinometer pattern used in which constant current is supplied to each strip and voltage is then measured using the same contacts (see also figure 2). The actinometers were prepared by first imprinting gold leads onto an alumina substrate. Silver was then vacuum evaporated onto the substrate to a thickness of 250 Å.

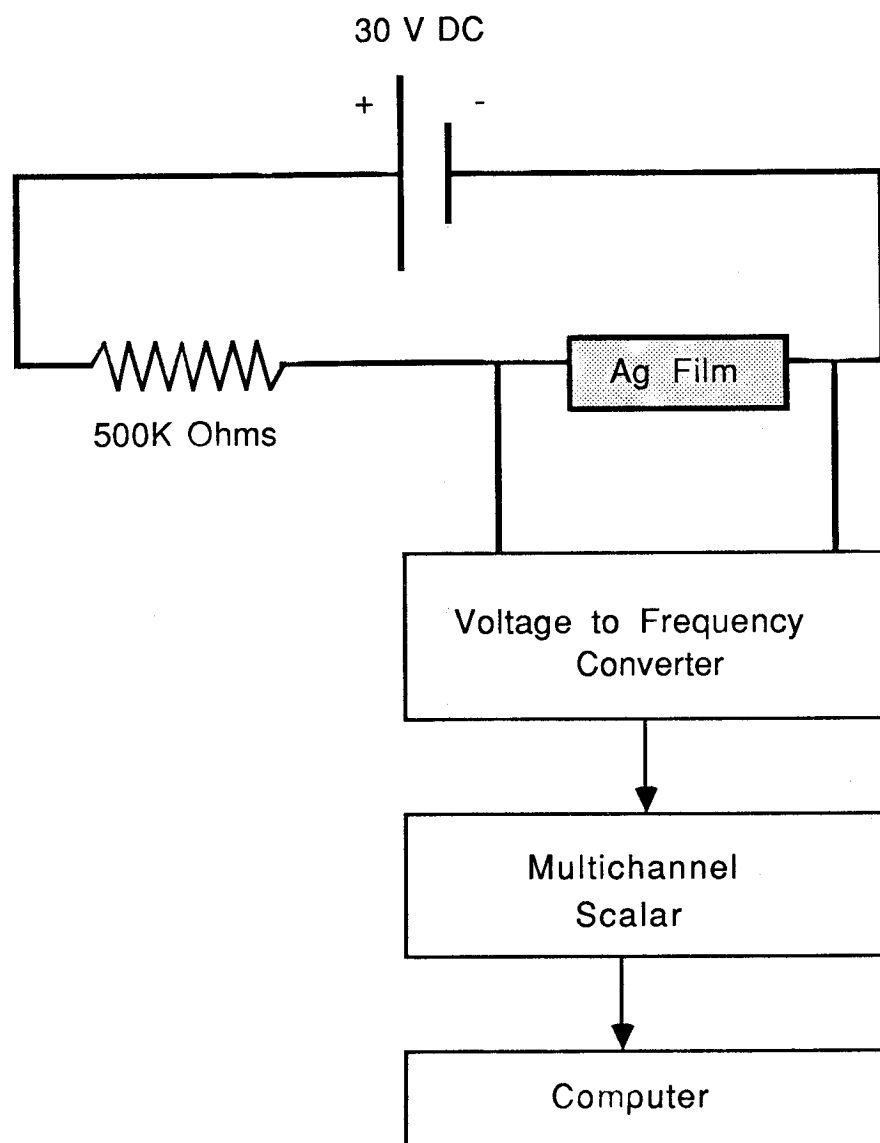


Figure 2. Electrical Circuit for Actinometer Resistance Measurements.

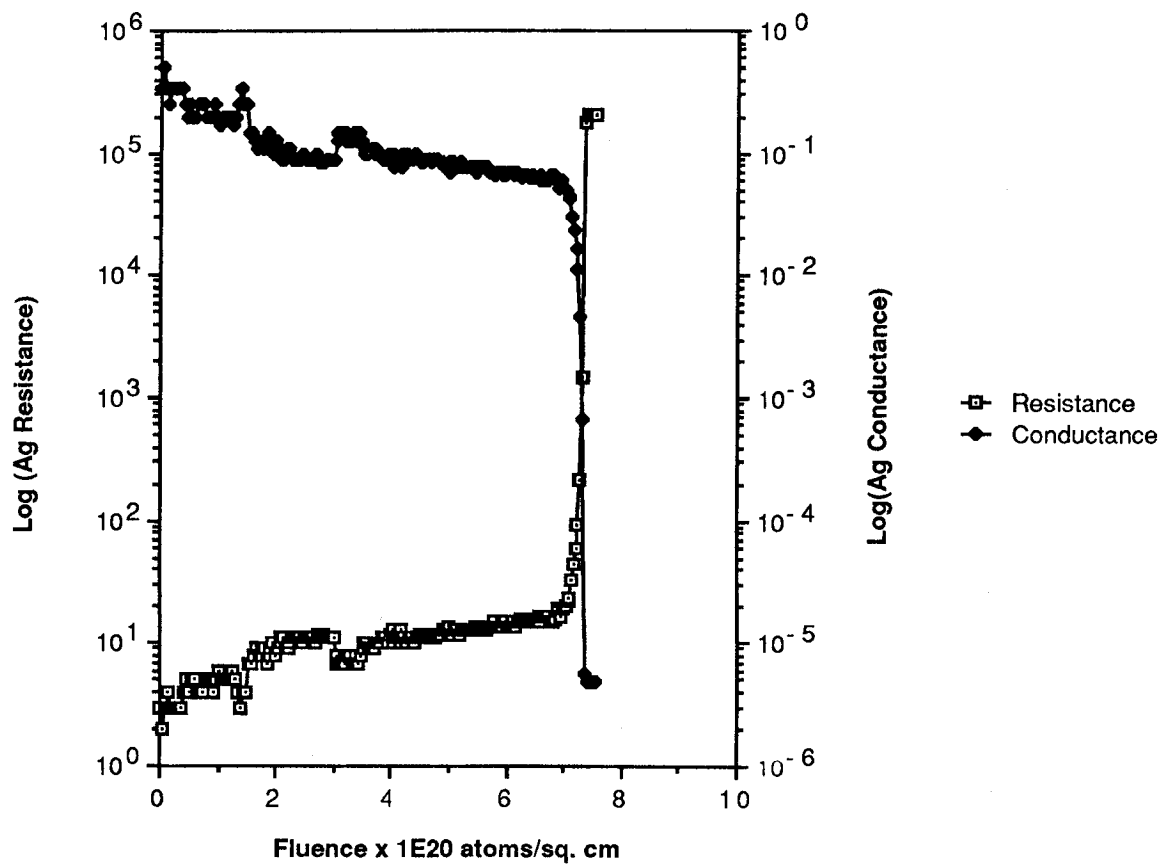


Figure 3. Plot of electrical resistance/conductance of silver underlying a protective coating (950 \AA SiO_2) shows the variation of $\log(\text{electrical resistance})$ and $\log(\text{electrical conductance})$ as a function of O-atom fluence. The shapes of the silver electrical resistance/conductance vs. fluence graphs do vary from coating to coating and from sample to sample of the same coating.

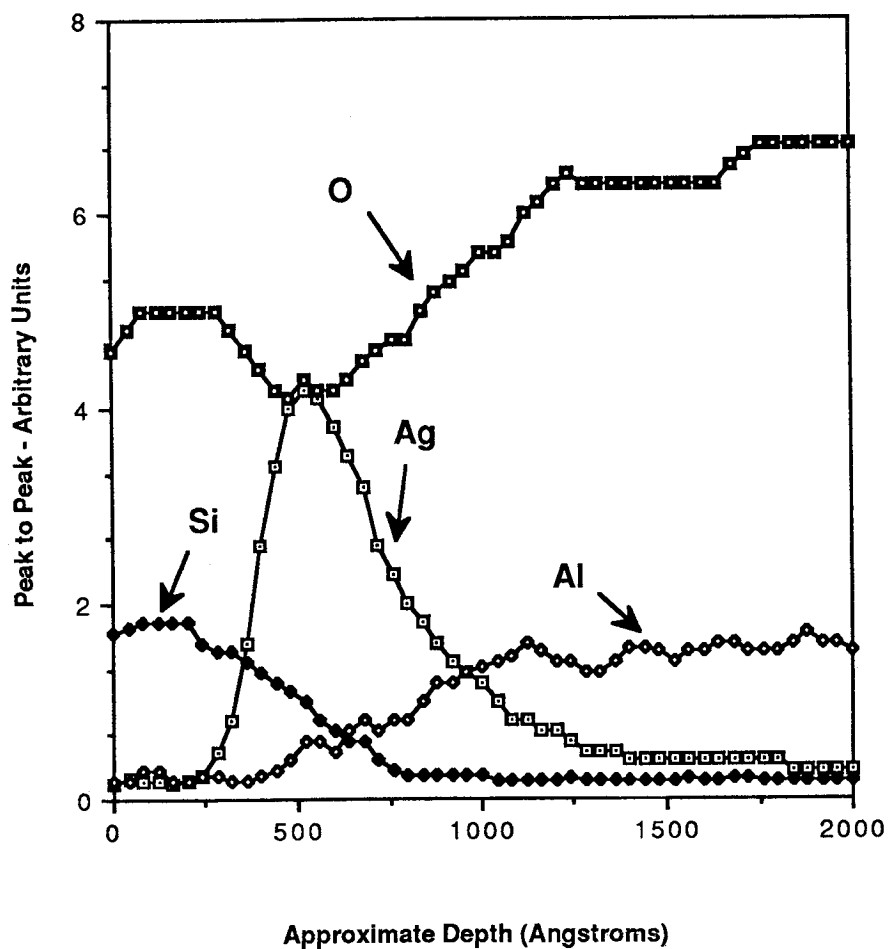


Figure 4. Auger elemental depth profile of Si, O, Ag, and Al in a SiO₂-coated silver actinometer after an O-atom exposure fluence of 11.0×10^{20} atoms/cm² shows that the SiO₂ coating was not eroded away. The actinometer has an alumina substrate, which accounts for the presence of Al. The depth is only an approximation, because it is based on an estimated sputtering rate.

Session IV

DYNAMIC TESTING

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